(19) THE JAPANESE PATENT OFFICE (JP)
(12) LAID-OPEN PATENT GAZETTE (A)
JP 9- 119079

(43) Publication date : May 6 , 19917 (H9)

(51) Int. Cl[6]	Identification No.	Office Class. No.	FI	Tech. displays Location
D0 6Q 1/10			D06Q 1/10	
D0 6M 17/00			D06N 3/00	
D06N 3/00			D06M 17/00	Z

Number of claims : 1
Number of pages : 5 (in the Japanese original)
Examination : Not requested

(21) Application No. : H7- 273995
(22) Dated : October 23, 1995(H7)

(71) Applicant: 0000054503
Unitika Co.
50, 1-chome, Higashi Honmachi,
Numazaki City, Hyogo Prefecture
(72) Inventors : K. Kamemaru et al.

(54) Title of the Invention

Printed Cloth Preparation With Recoverable Reflection

(57) [Summary]
[Objective] To provide a method of preparing soft feel printed cloth with recoverable reflection. Said cloth is durable to washing and has excellent recoverable reflection.

[Procedures] Upper hemisphere of the true spherical glass beads is submerged into the laminate surface between polyethylene film and film of heat resistance, followed by adding a light reflecting thin metal film. Afterwards,an adhesive of isocyanate is printed; a base fibrous material is thermally attached prior to the solidification of said adhesive, then the laminate and its non-printed part are peeled away.

[Scope Covered in The Invention]

We claim:

[Claim 1]
A method of preparing printed cloth with recoverable reflection. The preparation of said cloth consists of the following processes: the first process whereas (a) laminating a film having heat resistance of higher than 150 C and a polyethylene film to form a laminate and (b) spreading transparent and true spherical glass beads into laminate; the second process whereas (c) adding a light reflecting thin metal film ; the third process whereas (d) printing an adhesive of isocyanate containing 0.5- 10% of NCO and (e) thermally attaching a base fibrous material before solidifying said adhesive ; and the fourth process whereas (f) peeling away said laminate and its non-printed part.

[0001]
[Prior Art]

Conventionally, materials with recoverable reflection of excellent night viewing have been widely used to ensure the safety particularly at night. These recoverable reflection materials have the glass beads -type and the non-beads type. Among them, the glass beads-type material has become the main stream due to its excellent recoverable reflection . And, the glass beads-type has two types : the close type where glass beads are submerged in a resin layer and the open type where about half of the glass beads is exposed to the air.

[0002]

For the main applications , these recoverable reflection materials are used in the road signs where a recoverable reflection sheet is laminated to other object which is installed with

an adhesive layer at its back surface. The materials can also be used in safety clothes of the construction workers and policemen where base fibrous materials are used. Recently, due to the increasing concerns in the safety, as a measure of traffic accident prevention for the pedestrians and joggers , one starts using the cloth with recoverable reflection in window breakers and training wears. And its is expected that the demand will be increasing in the future.

[0003]

The recoverable reflection cloth of the close type has faced the following problems : it is a multi-layered structure of (1) front resin layer, (2) glass beads summersion layer, (3) focussing resin layer , (4) reflective layer , (5) adhesive layer, and (6) fibrous base . Therefore, although the cloth exhibits comparatively a good recoverable reflection, it would be difficult to obtain cloth with excellent recoverable reflection. Besides, the feel is extremely hard. With respect to these problems, one has proposed a simpler structure of (1) glass beads, (2) reflective layer, (3) adhesive layer and (4) fibrous base. In this structure, since glass beads are exposed to the air, the cloth has a better recoverable reflection and softer feel than the close type material. However, the cloth does not have the soft feel required for the cloth applications. In addition, the glass beads fall off in washing and dry cleaning. As a result, the cloth has encountered some drawbacks such as degradation in recoverable reflection and generation of apparent defects. Therefore, there is an increasing demand in cloth with recoverable reflection which has soft feel and is durable to washing.

[0004]
[Problems To Be Solved]

Under the aforementioned circumstance, the objective of this

invention is to provide a method of preparing a open-type printed cloth with excellent recoverable reflection which has soft feel and is durable to washing.

[0005]
[Procedures To Solve the Problems]

We have come up with a method of preparing printed cloth which is able to meet the aforementioned objective. Preparation of said cloth consists of the following processes: the first process whereas (a) laminating a film having heat resistance of higher than 150 C and a polyethylene film to form a laminate and (b) spreading transparent and true spherical glass beads into laminate; the second process whereas (c) adding a light reflecting thin metal film ; the third process whereas (d) printing an adhesive of isocyanate containing 0.5- 10% of NCO and (e) thermally attaching a base fibrous material before solidifying said adhesive ; and the fourth process whereas (f) peeling away said laminate and its non-printed part.

[0006]
[Configuration of Realizing This Invention]

We will described in details the present invention. First of all, in the first process, transparent and true spherical glass beads are spread on the polyethylene surface of a laminate which is formed by laminating a film having heat resistance of higher than 150 C and a polyethylene film. Upper hemisphere of said glass beads is submerged. Here, film having heat resistance of higher 150 C can be of any film which does not show any anomalous expansion and contraction and softening at the temperature beyond 150 C. The concrete examples are polyethylene terephthalate film, polychlorotrifluoroethylene film, polytetrafluoroethylene film , nylon strengthened with filler such as glass and phenol resin film or paper. From the point of view of cost and simplicity, polyethylene terephthalate is the most suitable material for the application in this invention.

[0007]

High density polyethylene film, medium density polyethylene film , low density polyethylene film and ethylene vinylacetate copolymer film can be used for the polyethylene film in this invention. However, from the point of view of low thermal softening point and low cost, in this invention, it would be most appropriate to use a low density polyethylene film . In this invention, one employs a laminate (hereinafter, called as the process film) which is formed by laminating a film having heat resistance of higher than 150 C and a polyethylene film. The method for forming this process film is as follows : polyethylene film is activated by being treated with corona discharge or plasma discharge, and then laminated with an adhesive.

[0008]

In this invention, the upper hemisphere , i.e. 40-60% of the glass bead diameter , of the transp[arent and true spherical glass beads is submerged onto the polyethylene film surface of the aforementioned process film. Here, the transparent and true spherical glass beads are prepared by made a glass chunk into true spheres , using the spraying sphere method and the rotary kirun? sphere method. The glass chunk is made from the material which has an index of refraction of 1.8-2.0 and consists of one or a combination of for example TiO2, SiO2, BaO, ZnO, CaO, PbO , Na_2O and the like. Preferred is the glass beads with an index of refraction of 1.90-1.94 having TiO2, BaO and ZnO as the main component.

[0009]

The procedure of submerging glass beads is as follows: glass beads, in a fine replenishing state, is attached to the surface of a polyethylene film which is softened at a temperature range of 80-150 C; afterwards, at a temperature range of 150- 200 C, the glass

beads are either sunk by their own weight or by an applied pressure . Method of submersing the glass beads can be conveniently chosen . At a submersion rate of less than 40% or more than 60%, the exposure rate to the air of the transparent glass beads upon the separation of the process film would be in the range of less than 40% or above 60%. At less than 40%, the recoverable reflection would be degraded; particulalrly, the angle characteristic at a large incident angle of the light would become poor. On the other hand, at above 60%, as will be discussed later, the glass beads would be peeled away easily from the adhesive layer, leading to the degradation in durability. Sphere diameters of the glass beads employed in this invention are in the range of 20- 100 microns. When the sphere diameter is less than 20 microns, recoverable reflection would be deteriorated and therefore this size of diameter is undesirable. On the other hand, at a sphere diameter of beyond 100 microns, thickness of the thus obtained cloth would be large and the feel would not be good and therefore undesirable.

[0010]

In this invention, for the second process, the upper hemisphere of the aforementioned glass beads are submerged and attached with a light reflecting metal film. The method of adding metal film having light reflection can be any of the deposition processes : evaporation or spruttering of reflective metal such as platimum. The thin film depostion is done at a high vacuum level of 10-2 Torr, using a vaccum evaporator where the metal is heated , evaporated and deposited, or ion beam or magnetron sputtering apparatus where a metal target is sputtered. In view of the cost and process simplicity, vacuum evaporation of aluminium is the most appropriate. Thickness of the coated film is preferably above 300 Angstrom, more preferably at above 500 Angstroms. When the film thickness is above 500 Angstroms, not only most of the light can be transmitted, but an entire reflection can also be made.

[0011]

For the third process in this invention, isocyanate adhesive containing 5-10% of NCO is printed on the aformentioned thin metal film; and a base fibrous material is thermally attached before solidifying the adhesive. Here the isocyanate adhesive is the material whereby the isocyanate group contains more than two functional groups in the molecule. To be concrete, the materials can be the the additive reacting materials with the compounds (for example trimethylose propane, glycerin, polyethylene glycol) containing active hydrogens with oligomers or monomers of for example : 2.4-toluene diisocyanate, 2.6-toluene diisocyanate, methylene bis (p-phenylene diisocyanate), 1.6- hexamethylene diisocyanate, isophorone diisocyanate, 1.5-naphthalene diisocyanate, ethylbenzene- alpha- 2.diisocyanate, 4.4'.4''- triphenylmethane triisocyanate and the like.

[0012]

The aforementioned isocyanate adhesive can be in the form where isocyanate groups are free, the adhesive can be stabilized by adding phenol, methylethylketooxium, or can also be in a form where with the later heat treatment, the isocyanate group appears. In addition, one can also add additives such as a replenishing agent which does not react with isocyanate or other materials. Forms of the adhesive can be either a soluble form or insoluble form and can be conveniently selected according to the operability and the applications. Content of NCO which is the reactive remaining group in the isocyanate compound is preferably in the range of 0.5- 10%. At a NCO content of less than 0.5%, washing durability of the printed cloth would not be enhanced. On the other hand, when NCO content exceeds 10%, feel of the printed cloth with recoverable reflection would be too hard, causing the easy rupture at the front surface during the course of wearing or washing. The NCO content mentioned here is the number represented by the following formula.

NCO content = (NCO remaining group in molecules x42) /molecular weight x 100

[0013]

In this invention, the aforementioned isocyanate adhesive is printed in such a manner that the drying film thickness would be in the range of 10- 70 microns. When the drying thickness is less than 10 microns, a soft feel would be obtained; however washing durability would be degraded. On the other hand, when the drying thickness is above 70 microns, the printed patterns would get blurred and the feel would become hard, which is not desirable. The printing method can be done using the commonly known printing apparatus, for example gravure roll coater, flat screen printing apparatus and rotary screen printing apparatus.

[0014]

In this invention, after printing the isocyanate adhesive, a base fibrous material is thermally attached prior to the solidifation of the adhesive. When the thermally attachment is realized after solidification of the adhesive, holding of the fibrous material ionto the adhesive would be weak. As a result, it would be difficult to obtain an excellent adhering force. Temperature of the thermally attachment depends on the pressing time and the method and is generally preferred to be below 170 C. When the thermal attachment is carried out at a temperature beyond 170 C, the process film, particularly the polyethylene film would have a large expansion and contraction , which is undesirable. In this thermal attachment, it is acceptable that the fibrous material is attached in advance with pressing , then followed by a thermal process. The attachment method can be the common methods such as the roll pressing or the flat pressing method.

[0015]

In this invention, the base fibrous materials can be any of the followings: polyamide synthetic fiber represented by nylon 6 and nylon 66, polyester synthetic fiber represented by polyethyleneterephthalate polyacrylonitrile synthetic fiber, polyvinylalcohol synthetic fiber, nylon 6/cotton or semi-synthetic fiber of for example triacetate, nonwovens, knitwork and fabric comprising mixed yarn fiber of for example polyethyleneterephthalate/ cotton. After the thermal attachment of the base fibrous material, aging is carried out for a constant period of time. Afterwards, in the fourth process, with the peeling-away of the process film and the non-printed part at the same time, one is able to obtain the printed cloth with recoverable reflection claimed in this invention.

[0016]
[Operation]

The isocyanate adhesive shows an extreme strong chemical reactivity with respect to the compound which contains active elements. Therefore, direct chemical coupling (first coupling) to the compound containing such functional group is formed, and excellent adhesion is obtained , where mechanically severing is difficult. When this isocyanate adhesive is directly printed and thermally attached on a light reflecting thin metal film , together with adhering solidly to the thin metal film, thickness of the thin metal film is in the order of submicrons at the most; this adhesive will adhere strongly even to the transparent and true spherical glass beads. Consequently, even with the dry cleaning of perfluoroethylene in the houshold cleaning operations, the glass beads and thin metal films would not fall off that easily; and one is able to obtain a recoverabale reflecting printed cloth which is durable to washing. The recoverable reflecting printed cloth prepared by the method of the present invention exhibits a soft feel. This is due to the fact that the adhesive is printed on the thin

metal film and with its attachment to the base fibrous material , permeation of the adhesive inwards the fibrous material would be prevented from happening.

[0017]
[Examples]

The present invention will now be described in details with reference to the following examples. Measurements and evaluation of the properties of the cloth in the examples were carried out, using the following methods.

(1) Washing Experiments

10, 20 washings were carried out, following the JIS L-0217 (103 code).

(2) Recoverable Reflection Characteristic

The reflection luminance of the pre-washing samples and after 10 washings , 20 washings with the washing experiments based on the aforementioned item (1) were measured (observing angle 0.33° , incident angle 5° and 40°).

[0018] (3) Change in Appearance

Variation in the appearance of the pre-washing samples and after 10 washings , 20 washings with the washing experiments based on the aforementioned item (1) were observed with naked eyes; and the relative judging evaluation was made with the following three stages.

○ ; almost no change in the appearance
△ ; a slight change in the appearance
× ; large falling-off of glass beads and evaporated aluminium film
< ; Poor appearance

(4) Feel

Relatively, three following evaluation stages were carried out, depending on the handling.

○ ; soft
△ ; a little bit hard
× ; hard

[0019] Example 1

First of all, for the base fibrous material, polyester filament 150 Denyl/36 filament was used, in a fawn structure 22 gauges knitting was made, refined and died using the common method (manufactured by NihonKayaku Co., dispersing dye Kayalon Fast Yellow GL 1% owf).

[0020]

Next, 50 microns polyethyleneterephthalate film and 40 microns low density polyethylene film were prepared. Treatment of the polyethylene film was realized, using a corona discharge treatment apparatus (manufactured by Kasuga Denki KK.). 30 KHz HFSS-101 type and III type electrode were used for the high frequency power supply and the discharge electrode, respectively. The corona electric discharge at a discharge energy of 20000 Joules/cm^2 was carried out. On the other hand, gravure coating was used for the polyethylene terephthalate films, high bond 703 1 L (manufactured by Hitachi Kasei Polymer Co., with toluene as the main solvent, 20% solid concentration low density polyester adhesive solution) was coated with 15 g/m^2 and dried and then laminated to the corona treeated surface of the aforementioned polyethylene film. And the process film was obtained.

[0021]

Furthermore, the aforementioned process film was first of all heat treated at 110 C for 3 minutes. At the side of the softened

polyethylene film, HI-53-105S (manufactured by Nihon Denki Glass Co., transparent glass beads with recoverable reflection of a sphere diameter of about 60 microns, index of refraction of 1.92 with TiO_2 and BaO as the main components) was attached in a single layer in a fine replenishing form. Next, the heat treatment was realized at 170 C for 3 minutes. Glass beads inside the softened polyethylene film was submerged to about half way by its own weight. Next, a vacuum evaporator was employed, at a vacuum of 10^{-4} Torr, aluminium of a thickness of 800 Angstroms was coated on the exposure surface of the aforementioned glass beads , using the vacuum evaporation to form a reflective film.

[0022]

Afterwards, Polynate 955H(manufactured by Toyo Polymer Co., NCO content of 1.5%, isocyante adhesive solution with 50% solid) was printed on the aforementioned aluminium evaporated surface, , using a flat screen printing apparatus in a checkered pattern of an 1 cm angle unit to a thickness of 70 microns (drying thickness of 35 microns), and then laminated at 100 C for 1 minute. Aterwards, thermal attachment to the aforementioned base fibrous material was made at a pressure of 2 Kg/ cm^2 for 5 seconds in a hot press at 150 C. Two days later, the process film and the non printed part were peeled away. And the recoverable reflecting printed cloth claimed in this invention was obtained.

[0023]

In the purpose of comparing with the results of the experiments of the present invention, the printed cloth with recoverable reflection as described in the following comparative examples was made.

[0024] [Comparative Example 1]

In the submersion process (the first process) of glass beads

in the polyethylene film in example 1, indutive heat generating jacket roll (Tokuden KK.) at a control level at 150 C was nipped with a metal roll at a pressure of 10 kg/cm. Except that one selected a method whereby about 65% of the glass beads were submerged, other procedures remained the same as the ones in example 1 . And a recoverable reflecting printed cloth with an air exposure of 65% was obtained.

[0025] [Comparative Example 2]

The process film in example 1 was heat treated at 150 C for 2 minutes instead of at 170 C for 3 minutes; and besides the fact that about 35% of the glass beads was submerged, other procedures remained essentially the same as the ones in example1. And recoverable reflective printed cloth with about 35% exposure of the glass beads was obtained .

[0026] [Comparative Example 3]

In example 1 for the isocyanate adhesive , Polynate 955 H was substituted with Polynate 74 (manufactured by Toyo Polymer Co., NCO content of 10.5%, isocyanate adhesive solution with 60% solid). Other procedures remained essentially the same as that in example 1. And printed cloth with recoverable reflection for comparison was obtained.

[0027] [Comparative Example 4]]

In example 1 for the isocyanate adhesive , Polynate 955 H was substituted with NCO free adhesive . Other procedures remained the same as that in example 1. And printed cloth with recoverable reflection for comparison was obtained.

Formula 1

Melcy (merusii??) 4241 100 parts
(manufactured by Toyo Polymer Co., polyurethane emulsion adhesive solution)

AC-C-65 3 parts
(manufactured by Toyo Polymer KK., eposy cross-linking agent)
AD-K-8 2 parts
(manufactured by Toyo Polymer KK., urethane adhesion promoting agent)

[0028] [Comparative Example 5]

In example 1 except that flat screen printing apparatus was used and a printing thickness of 15 microns was made (with a dry thickness of 8 microns) , other procedures remained the same as that in example 1. And printed cloth with recoverable reflection for comparison was obtained.

[0029] [Comparative Example 6]

In example 1 except that flat screen printing apparatus was used and a printing thickness of 150 microns was made (with a dry thicknbess of 875 microns) , other procedures remained the same as that in example 1. And printed cloth with recoverable reflection for comparison was obtained.

[0030]

The recoverable reflective printed clothes in the example and the comparative examples were measured and evaluated. The results are shown in Table 1.

[0031]
[Table 1]

	Reflection luminance at an incident angle of 5° and 40°※						Appearance Change		Feel
	no-washing		After 10 washings		After 20 washings		After 10 washings	After 20 washings	
	5°	40°	5°	40°	5°	40°			
This invention	367	383	359	357	347	350	○	○	○~△
Comparative Example 1	358	342	227	225	119	114	△~×	×	○~△
Comparative Ex. 2	357	221	350	216	341	210	○	○	○~△
Comparative Ex. 3	363	360	355	349	339	340	△	△	×
Comparative Ex. 4	365	364	313	298	251	237	△	×	○
Comparative Ex. 5	360	357	309	299	250	228	△	×	○
Comparative Ex. 6	364	362	350	351	337	335	○	○	×

※ Reflection luminance : Cd/lx/m²

[0032]

From Table 1, it is known that the recoverable reflecting printed cloth in this invention, as compared with the printed cloth comparative examples 1-6, shows excellent luminance , soft feel and is durable to washing .

[0033]
[Effect of the Invention]

According to the method claimed the present invention, one is able to obtain a recoverable reflecting printed cloth which has an excellent recoverable reflection and is durable to washing. The recoverable reflective printed cloth in this invention is of an open type where glass beads of a relatively simple structure in the recoverabkle reflection is exposed to air; therefore, one is able to prepare a simple , yet low cost structure. Furthermore, the cloth has also excellent soft feel which is indispensable for the clothing materials. The recoverable reflecting printed cloth of this invention , from the above-mentioned characteristics, is a suitable material for safety wearing materials and sports materials.